

LIQUID NON AQUEOUS OR SUBSTANTIVE NON AQUEOUS
LAUNDRY DETERGENT COMPOSITION"

5 The present invention relates to liquid non aqueous
or substantially non aqueous laundry detergent
compositions.

 Liquid nonaqueous heavy duty laundry detergent
compositions are well known in the art. For
10 instance, compositions of that type may comprise a
liquid nonionic surfactant in which are dispersed
particles of a builder, as shown for instance in
U.S. Patents Nos. 4,316,812; 3,630,929; 4,264,466,
and British Patent Nos. 1,205,711 and 1,270,040.

15 In the ordinary use of European household
automatic washing machines, the user places the
laundry detergent composition in a dispensing unit
(e.g. a dispensing drawer) of the machine. Then
during the operation of the machine, the detergent
20 in the dispenser is subjected to a stream of cold
water to transfer it to the main body of wash
solutions. In winter, when the detergent
composition and the water fed to the dispenser are
cold, there can be problems in that some of the
25 composition is not flushed completely off the
dispenser during operation of the machine, and a
deposit of the composition builds up with repeated
wash cycles, so that it may become necessary for the
user to flush the dispenser with hot water.

30 One reason for this problem involves the
behaviour of the nonionic surfactant when mixed with
cold water. Its viscosity increases markedly and a

5 gel is formed. As a result, the detergent composition does not flow readily or completely from the dispenser.

10 It has now been found that the flow from the dispenser can be improved considerably by including in the liquid detergent composition a nonionic surfactant which has been modified to convert a free hydroxyl group thereof to a moiety having a free carboxyl group. Such a compound may be formed, for instance, by reacting a nonionic surfactant with a
15 polycarboxylic acid anhydride, such as succinic anhydride, to form a partial ester of the polycarboxylic acid. The resulting acidic compound will react, in the wash bath, with the alkalinity of the detergent composition and acts as an effective
20 anionic surfactant.

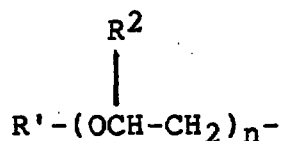
Thus according to the present invention a liquid non aqueous or substantially non aqueous heavy duty laundry detergent composition comprising a suspension of builder salt in a liquid nonionic
25 surfactant, the said composition containing a polyether carboxylic acid to decrease the temperature at which the said surfactant forms a gel with water.

The acidic compound is thus a carboxylic acid moiety joined to the residue of the nonionic surfactant by
30 a carboxylic ester linkage. Instead of a succinic acid moiety, other polycarboxylic acid moieties may be used, e.g. maleic, glutaric, malonic, phthalic or citric acid moieties. In broader aspects of the present invention, other linkages may be used, such

as ether, thioether or urethane linkages, formed by conventional reactions. For instance, to form an ether linkage, the nonionic surfactant may be treated with a strong base (to convert its OH group to an ONa group for instance) and then reacted with a halocarboxylic acid such as chloroacetic acid or chloropropionic acid or the corresponding bromo compound. Thus the resulting carboxylic acid may have the formula $R-Y-ZCOOH$ where R represents the residue of a nonionic surfactant (on removal of a terminal OH), Y represents an oxygen or sulphur atom and Z represents an organic linkage or group such as a hydrocarbon group of say, one to ten carbon atoms which may be attached to the oxygen (or sulphur) atom of the formula directly or by means of an intervening linkage or group such as an oxygen-containing linkage or group,

e.g. a $\overset{\text{O}}{\parallel}{-C-}$ or $\overset{\text{O}}{\parallel}{-C-NH-}$, (i.e. a carbonyl or carboximido group, respectively).

In another aspect of the present invention, the carboxylic acid may be produced from a polyether which is not a nonionic surfactant, e.g. it may be made by reaction with a polyalkoxy compound such as polyethylene glycol or a monoester or monoether thereof which does not have the long alkyl chain characteristic of the nonionic surfactants. Thus, R may have the formula:



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where R^2 represents a hydrogen atom or a methyl group, R^1 represents an alkylphenyl group or an alkyl group or other chain terminating group and "n" is at least 3 such as 5 to 25. When the alkyl group of R^1 is a higher alkyl group, R represents a residue of a nonionic surfactant. As indicated above R^1 may instead be a hydrogen atom or a lower alkyl group (e.g. a methyl, ethyl, propyl or butyl group) or a lower acyl group (e.g. an acetyl group). The acidic polyether compound is preferably present, in the detergent composition, as a solution in the nonionic surfactant.

The carboxylic acid compound used may instead be a polyalkoxycarboxylate or N-acyl sarcosinate as

described and listed in Kirk-Othmer, "Encyclopedia of Chemical Technology", 3rd Edition, Vol. 22 (1983), Pages 348-349.

- As is well known, the nonionic synthetic
5. organic detergents are characterised by the presence of an organic hydrophobic group and an organic hydrophilic group and are typically produced by the condensation of an organic aliphatic or alkyl aromatic hydrophobic compound with ethylene oxide
 10. (hydrophilic in nature). Practically any hydrophobic compound having a carboxy, hydroxy, amido or amino group with a free hydrogen attached to the nitrogen atom can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene
 15. glycol, to form a nonionic detergent. The length of the hydrophilic or polyoxyethylene chain can be readily adjusted to achieve the desired balance between the hydrophobic and hydrophilic groups. Typical suitable nonionic surfactants are those
 20. disclosed in U.S. Patents 4,316,812 and 3,630,929, as well as those described and listed in the discussion on nonionic surfactants in Kirk-Othmer "Encyclopedia of Chemical Technology", 3rd Edition, Vol. 22 (1983), pages 360-379.
 25. The compositions according to the present invention preferably contain fine particles of a detergent builder dispersed in the nonionic surfactant. Among the suitable builders are inorganic and organic builder salts such as the
 30. phosphates, carbonates, silicates, phosphonates,

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polyhydroxysulphonates, polycarboxylates and the like. Typical suitable builders are those disclosed in U.S. Patents 4,316,812; 4,264,466; and 3,630,929.

5 The present invention also extends to a liquid non aqueous or substantially non aqueous heavy duty laundry detergent composition comprising a suspension of a builder salt in a liquid nonionic surfactant, the said composition containing also a compound comprising nonionic surfactant in which a
10 hydrogen atom has been replaced by a group having a free -COOH group.

Since, as will be observed below from Example 4, the compositions of the present invention may be used at relatively low dosages, it is desirable to
15 supplement any phosphate builder (such as sodium tripolyphosphate) with an auxiliary builder such as a polymeric carboxylic acid having high calcium binding capacity, in an amount in the range, for instance, of about 1 to 10% of the composition, to
20 inhibit incrustation which could otherwise be caused by formation of an insoluble calcium phosphate. Such auxiliary builders are well known in the art.

The composition preferably comprises a peroxygen bleaching agent. This may be a peroxygen
25 compound, such as an alkali metal perborate, percarbonate or perphosphate; a particularly suitable material is sodium perborate monohydrate. The peroxygen compound is preferably used in admixture with an activator therefor. Suitable
30 activators are those disclosed in U.S. Patent 4,264,466 or in column 1 of U.S. Patent 4,430,244. Polyacylated compounds are preferred activators;

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among these, compounds such as tetraacetyl ethylene-
5 diamine ("TAED") and pentaacetyl glucose are parti-
cularly preferred.

The activator usually interacts with the
peroxygen compound to form a peroxyacid bleaching
10 agent in the wash water. It is preferred to include

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- a sequestering agent of high complexing power to inhibit any undesired reaction between such peroxy-acid and hydrogen peroxide in the wash solution in the presence of metal ions. Such a sequestering agent is an organic compound which is able to form a complex with Cu^{2+} ions, such that the stability constant (pK) of the complexation is equal to or greater than 6, at 25°C, in water, of an ionic strength of 0.1 mole/litre, pK being conventionally defined by the formula: $\text{pK} = -\log K$ where K represents the equilibrium constant. Thus, for example, the pK values for complexation of copper ion with NTA and EDTA at the stated conditions are 12.7 and 18.8, respectively. Suitable sequestering agents include the sodium salts of nitriloacetic acid (NTA); ethylene diamine tetraacetic acid (EDTA); diethylene triamine pentaacetic acid (DETPA); diethylene triamine pentamethylene phosphonic acid (DTPMP); and ethylene diamine tetramethylene phosphonic acid (EDITEMPA).

- Other ingredients which may be included in the compositions of the present invention are enzymes (e.g. proteases, amylases or lipases or mixtures thereof), optical brighteners, antiredeposition agents, and colourants (e.g. pigments or dyes).

- The compositions of the present invention may also contain an inorganic insoluble thickening agent or dispersant of very high surface area such as finely divided silica of extremely fine particle size (e.g. of 5-100 millimicrons diameter such as

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5 sold under the name Aerosil (Registered Trade
Mark))? or the other highly voluminous inorganic
carrier materials disclosed in U.S. Patent
3,630,929, in proportions of 0.1-10%, e.g. 1 to 5%.
It is preferable, however, that compositions which
10 form peroxyacids in the wash bath (e.g. compositions
containing peroxygen compound and activator
therefor) be substantially free of such compounds
and of other silicates; it has been found, for
instance, that silica and silicates promote the
undesired decomposition of the peroxyacid.

15 In a preferred form of the present invention
the mixture of liquid nonionic surfactant and solid
ingredients is subjected to an attrition type of
mill in which the particle sizes of the solid
ingredients are reduced to less than about 10
20 microns, e.g. to an average particle size of 2 to 10
microns or even lower (e.g. 1 micron). Compositions
whose dispersed particles are of such small size
have improved stability against separation or
settling on storage. It is found that the acidic
25 polyether compound can decrease the yield stress of
such dispersions, aiding in their dispensibility,
without a corresponding decrease in their stability
against settling.

30 The mixture may contain anti-settling
ingredients such as a partial ester of phosphoric
acid and a higher alkanol, present in small amounts
such as less than 1%, e.g. below 0.5%, during the
grinding. Other phosphate ester surfactants may be
used instead such as those described and listed in

Kirk-Othmer "Encyclopedia of Chemical Technology",
3rd Edition, Vol. 22 (1983), pages 359-361.

- In the grinding operation it is preferred that the proportion of solid ingredients be high enough
5. (e.g. at least about 40% such as about 50%) that the solid particles are in contact with each other and are not substantially shielded from one another by the nonionic surfactant liquid. Mills which employ grinding balls (ball mills) or similar mobile
 10. grinding elements have given very good results. Thus, one may use a laboratory batch attritor having 8 mm diameter steatite grinding balls. For larger scale work a continuously operating mill in which there are 1 mm or 1.5 mm diameter grinding balls
 15. working in a very small gap between a stator and a rotor operating at a relatively high speed (e.g. a CoBall mill) may be employed; when using such a mill, it is desirable to pass the blend of nonionic surfactant and solids first through a mill which
 20. does not effect such fine grinding (e.g. a colloid mill) to reduce the particle size to less than 100 microns (e.g. to about 40 microns) prior to the step of grinding to an average particle diameter below about 10 microns in the continuous ball mill.
 25. In the compositions of the present invention, typical proportions of the ingredients are as follows:

Suspended detergent builder, within the range of about 10 to 60% such as about 20 to 50%, e.g.

30. about 25 to 40%;

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Liquid phase comprising nonionic surfactant and dissolved carboxylic acid gel-inhibiting compound, within the range of about 30 to 70%, such as about 40 to 60%; this phase may also include a diluent

5. such as a glycol, e.g. polyethylene glycol (e.g. "PEG 400") or hexylene glycol.

Carboxylic acid gel-inhibiting compound, an amount to supply in the range of about 0.5 to 10 parts (e.g. about 1 to 6 parts such as about 2 to 5

10. parts) of -COOH (M.W. 45) per 100 parts of blend of such acid compound and nonionic surfactant. (In Example 4 below there are about 3 parts of COOH per 100 parts of such blend). Typically, the amount of the carboxylic acid compound is in the range of

15. about 0.01 to 1 part per part of nonionic surfactant, such as about 0.05 to 0.6 part, e.g. about 0.2 to 0.5 part;

Peroxygen compound (such as sodium perborate monohydrate) in the range of about 2 to 15%, such as

20. about 4 to 10%;

Activator, in the range of about 1 to 8%, such as about 3 to 6%.

A sequestering agent of high complexing power, in the range of about 0.25 to 3%, such as about 0.5 to

25. 2%.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples.

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EXAMPLE 1

This examples describes the preparation of a flow improving acidic compound from a nonionic detergent and succinic anhydride.

5. 400 g of a nonionic surfactant which is a C₁₃ to C₁₅ alkanol which has been alkoxyated to introduce 6 ethylene oxide and 3 propylene oxide units per alkanol unit is mixed with 32 g of succinic anhydride and heated for 7 hours at 100°C. The
10. mixture is then cooled and filtered to remove unreacted succinic material. Infrared analysis indicates that about one half of the nonionic surfactant has been converted to the acidic half ester thereof. Viscosities and gel temperatures of
15. the product as compared to the unmodified nonionic surfactant are given in Table 1 below;

TABLE 1

	<u>Product</u>	<u>Unmodified Non-ionic Surfactant</u>
20. Viscosity at 20°C	138 cps	60 cps
Gel temperature of a 40/60 mixture with water (i.e. mixture containing 60% water)	7°C	20°C
25. Viscosity of the 40/60 mixture with water		
at 25°C	60 cps	189 cps
at 20°C	100 cps	445 cps

- It will be seen that even though the product
30. (which, as previously indicated, is a mixture of

about equal parts of unmodified nonionic surfactant
5 and acidic half ester thereof) has a higher
viscosity than the unmodified surfactant, its
viscosity on dilution with water is considerably
lower, as is its gelling temperature.

EXAMPLE 2

10 This example describes the preparation of a
flow improving acidic compound from a nonionic
detergent and succinic anhydride.

522 g of the nonionic surfactant known as
Dobanol (Registered Trade Mark) 25-7 (the product of
15 ethoxylation of a C₁₂ to C₁₅ alkanol, which product
has about 7 ethylene-
oxide units per molecule of alkanol) is mixed with
100 g of succinic anhydride and 0.1 g of pyridine
(which acts as an esterification catalyst here) and
20 heated at 60°C for 2 hours, cooled and filtered to
remove unreacted succinic material. Infrared
analysis indicates that substantially all the free
hydroxyls of the surfactant have reacted.

Other esterification catalysts, such as an
25 alkali metal alkoxide (e.g. sodium methoxide) may be
used in place of, or in admixture with, the pyridine.

EXAMPLE 3

Example 2 is repeated using 1000 g of Dobanol
91-5 (the product of ethoxylation of a C₉ to C₁₁
30 alkanol, which product has about 5 ethylene oxide
units per molecule of alkanol) and 265 g succinic
anhydride.

EXAMPLE 4

This is an example of a detergent composition

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in accordance with the present invention.

5 A liquid nonaqueous heavy duty laundry detergent is formulated from the following ingredients, in the proportions specified.

35% nonionic surfactant comprising a mixture of equal parts of:

10 (a) a relatively water soluble nonionic surfactant which forms a gel when mixed with water at 25°C, specifically a C₁₃ to C₁₅ alkanol which has been alkoxylated to introduce 10 ethylene oxide and 5 propylene oxide units per alkanol unit and

15 (b) a less water-soluble nonionic surfactant, specifically a C₁₃ to C₁₅ alkanol which has been alkoxylated to introduce 4 ethylene oxide and 7 propylene oxide units per alkanol unit.

12% of the product of Example 3.

20 31.2% sodium tripolyphosphate.

9% sodium perborate monohydrate.

4.5% tetraacetylenediamine; this is an activator for the sodium perborate.

25 4% copolymer of about equal moles of methacrylic acid and maleic anhydride, completely neutralized to form the sodium salt thereof (Sokalan CP5); this serves to inhibit incrustation (as from formation of dicalcium phosphate).

30 1% sodium salt of diethylene triamine penta-methylene phosphonic acid (DTPMP).

1% Proteolytic enzyme slurry (in nonionic surfactant (Esperase (Registered Trade Mark))).

1% mixture of sodium carboxymethylcellulose and

5 hydroxymethylcellulose (an antiredeposition agent)
 (Relatin DM4096).

 0.5% perfume.

 0.5% optical brightener.

 0.3% partial ester of phosphoric acid and a C₁₆
 to C₁₈ alkanol (Empiphos (Registered Trade Mark)
10 5632, in which there is about 1/3 monoester and 2/3
 diester).

 The ingredients are mixed together, with the
 phosphoric ester and then the sodium tripolyphosphate
 being preferably added last, and passed through a
15 colloid mill to reduce the particle size of the
 solid materials to less than 100 microns (e.g. to
 about 40 microns). The mixture is then subjected to
 grinding to reduce the sizes of the suspended solid
 particles to less than 10 microns (e.g. to in the
20 range of about 2 to 10 microns with less than about
 10% of the solids having particle sizes above about
 10 microns).

 The ingredients and conditions are chosen so
 that the total unbound water content of the
25 composition is less than 2%, preferably less than
 1%, such as about 0.5% or less.

 The mixture has a high viscosity, but dispenses
 readily with cold water in an automatic washing
 machine. Its specific gravity is about 1.25. It
30 gives excellent washing when used at a dosage of
 about 100 grams per wash load (as compared with 170
 grams per wash load for the usual heavy duty laundry
 detergent powders) in conventional European home
 laundry machines (which employ about 20 litres of

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water for the washing bath).

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It is to be understood that the foregoing detailed description is given merely by way of illustration and that variations may be made therein

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CLAIMS

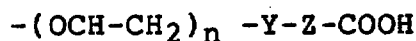
1. A liquid nonaqueous or substantially nonaqueous heavy duty laundry detergent composition comprising a suspension of builder salt in a liquid nonionic surfactant, the said composition containing a polyether carboxylic acid to decrease the temperature at which the said surfactant forms a gel with water.

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2. A composition as claimed in Claim 1 in which the said polyether carboxylic acid is soluble in the said nonionic surfactant.

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3. A composition as claimed in Claim 1 or Claim 2 in which the said polyether carboxylic acid contains a grouping of the formula



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R²

where R² represents a hydrogen atom or a methyl group, Y represents an oxygen or a sulphur atom and Z represents an organic linkage or group.

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4. A composition as claimed in Claim 1, 2 or 3 in which the said polyethercarboxylic acid is a half ester of a dicarboxylic acid and a nonionic surfactant.

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5. A composition as claimed in Claim 1, 2, 3 or 4 in which the proportion of the said polyether



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carboxylic acid is such as to provide about 0.5 to 10 parts of -COOH per 100 parts of the mixture of the said polyether carboxylic acid and the said nonionic surfactant.

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6. A liquid nonaqueous or substantially nonaqueous heavy duty laundry detergent composition comprising a suspension of a builder salt in a liquid nonionic surfactant, the said composition containing also a compound comprising nonionic surfactant in which a hydrogen atom has been replaced by a group having a free -COOH group.

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7. A composition as claimed in Claim 6 in which the said compound is a partial ester of a nonionic surfactant and a polycarboxylic acid.

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8. A composition as claimed in Claim 7 in which the said polycarboxylic acid is succinic acid.

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9. A composition as claimed in Claim 6 in which said compound is a partial ester of polycarboxylic acid and a polyethoxylated higher alkanol.

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10. A composition as claimed in any one of Claims 1 to 9 in which the said builder salt is an alkali metal polyphosphate.

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11. A composition as claimed in any one of Claims 1 to 10 containing also suspended peroxygen bleaching agent.



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12. A composition as claimed in Claim 11 in which the said bleaching agent comprises sodium perborate monohydrate and an activator therefor.

5 13. A composition as claimed in Claim 12 in which the said activator comprises tetraacetyl ethylene diamine.

10 14. A composition as claimed in any one of Claims 1 to 13 in which the particle size of the suspended builder salt is below about 10 microns.

15 15. A liquid heavy duty laundry detergent composition as claimed in Claim 6 substantially as specifically described herein with reference to Example 4.

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